CONDUCTIVITY, TEMPERATURE COEFFICIENT OF CONDUCTIVITY AND PERCENTAGE DISSOCIATION OF SOME RATHER UNUSUAL SALTS IN AQUEOUS SOLUTIONS.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

By

CHARLES WATKINS.

June, 1915.

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CONDUCTIVITY, TEMPERATURE COEFFICIENT OF CONDUCTIVITY AND PERCENTAGE DISSOCIATION OF SOME RATHER UNUSUAL SALTS IN AQUEOUS SOLUTIONS

HISTORICAL

This investigation is a contribution to the study of the conductivity, temperature coefficients of conductivity and dissociation of electrolytes in aqueous solutions. It is a continuation of the work begun by Jones and West[1] in 1905, and which has been in progress continuously since that time. After studying thirty-two substances, organic and inorganic, with special reference to the effects of temperature over a range from 0° to 35°, Jones and West reached the following conclusions:

1. A large increase in conductivity due to greater ionic mobility accompanies a rise in temperature.

2. A rise in temperature brings about a slight decrease in dissociation. This is in accord with the law of Dutoit and Aston, connecting the association of a solvent with its dissociating power, and is in harmony with the results of Ramsey and Shields, showing the relation between the dissociation of water and rise in temperature.

3. Temperature coefficients of conductivity expressed in percentage units decrease with rise in temperature.

4. The temperature coefficients of conductivity expressed in conductivity units, in the case of salts, increase with rise in temperature, while in the case of acids they decrease.

Jones and Jacobson[2] next took up this study, and after investigating 35 compounds over the same range of temperature used by West, found:

1. The molecular conductivity of electrolytes in aqueous solutions increase as a parabolic function of the temperature from 0° to 35°.

2. Hydrolysis is a source of error in obtaining the value of $\mu\infty$.

3. The conductivity of water is a linear function of the temperature.

1 Amer. Chem. Journ., 34, 357 (1905).
2 Amer. Chem. Journ., 40, 355, (1908).

4. Salts that are strongly hydrated in solution show greater increase in conductivity with rise in temperature than salts that are slightly hydrated.

Aqueous solutions of organic acids were the subject of several investigations by Jones and his co-workers. White,[3] while engaged in this work, found that the percentage temperature coefficients of conductivity of most of the organic acids examined were small, and decreased with rise in temperature and with increased dilution. The rate of decrease of these coefficients, expressed in conductivity units, with rise in temperature indicates that these acids are much less hydrated than mineral acids. In the case of the animo acids, the percentage coefficients of conductivity are very large. Internal salt formation was suggested as the cause of these high values. He also shows that the conductivity of most organic acids is a parabolic function of the temperature, but concludes that no general statement can be made concerning the change of dissociation with temperature change, since the behavior of solutions of organic acid is not in accord with the Thompson-Nernst hypothesis connecting dissociating power and dialectic constant.

Clover[4] continued this work, but over a wider range of temperature. Some measurements were made at a temperature of 80°. West[5] and Wightman[6] also did work in this field. The results obtained by these investigators were in accord with the finding of their predecessors.

Alum and other soluble salts were studied by Hosford and Jones.[6] They found that the conductivity of an alum is less than the conductivity of the constituent salts. This is evidence in favor of a theory advanced by Jones regarding the existence of double salts, as such, in concentrated solutions.

While studying the conductivity of a number of electrolytes in aqueous solutions, Winston and Jones[7] found apparent exceptions to the earlier work, viz., an increase in percentage dissociation with rise in temperature and large temperature coefficients when there were no indications of large hydration. This led Winston to advance the theory that inductive action takes place through the solvent between charged ions and neutral molecules, giving rise to complex molecules and ions in solution. Wightman,[8] Springer[9] and Smith[10] extended the work previously done

3 Amer. Chem. Journ., 42, 520, (1909).
4 Amer. Chem. Journ., 43, 187, (1910).
5 Ibid, 44, 508, (1910).
6 Ibid, 46, 56, (1911).
7 Ibid, 46, 368, (1911).
8 Amer. Chem. Journ., 48, 320, (1912).
9 Ibid, 48, 411, (1912).
10 Ibid, 50, 1, (1913).

in this laboratory on organic acids. The last named investigator found that Euler's equation

$$\mu_t = \mu_o + at - bt^2$$

holds in every case studied. He also calls attention to the fact that isomeric acids do not behave similarly with regard to change in dissociation. That the migration velocity of anions is a function of the number of atoms constituting the anion was indicated by his experimental work.

Howard[11] and Shaeffer[12] have each published papers on conductivity work carried out under the direction of Jones.

In this brief review of the conductivity studies made in this laboratory, attention has been called to work done only on aqueous solutions. Similar work has been done by Jones and his collaborators using glycerol, ethyl alcohol, and formamid as solvents. A considerable number of investigations involving various mixtures of different solvents have been carried out. For a full account of this work, Publications 80, 180, and 210 of the Carnegie Institution of Washington should be consulted.

11 Ibid, 48, 500, (1912).
12 Ibid, 49, 207, (1913).

EXPERIMENTAL

Apparatus.

Bridge and Rheostat.—All readings were made on an improved circular slide wire bridge constructed by the Leeds and Northrop Co., of Philadelphia. From a bridge of this type, readings can be made to a fraction of a millimeter. The resistance box had been recently standardized. The plugs of this piece of apparatus were kept clean by frequently rubbing them with a piece of soft chamois skin moistened with alcohol.

Cells.—The cells used were of the same type described and sketched in previous articles[13] on this subject. Since all cells used had been in service for several years, no trouble was experienced from the leaching out of soluble constituents from the glass. On account of the rather wide range of conductivities shown by the salts studied, it was impossible, in every instance, to use the same cell for the same dilution.

Constant Temperature Baths.—With the exception of the zero bath, constant temperature was maintained by the application of a principle developed in these laboratories by Professor Morse.[14] This is best described in his own words:

"If all the water or air in a bath is made to pass rapidly (1) over a continuously cooled surface which is capable of reducing the temperature slightly below that which it is desired to maintain, then (2) over a heated surface which is more efficient than the cooled one, but under the control of a thermostat, and (3) again over the cooled surface, etc., it should be practicable to maintain in the bath any temperature for which the thermostat is set, and the constancy of the temperature should depend only on the sensitiveness of the thermostat and the rate of flow of the water or air. The principle is a general one and provides for the maintenance of any temperature between zero and the boiling point of water."

The particular type of bath and thermostat used, was described fully by Davis and Putnam in Publication No. 210 of the Carnegie Institution of Washington. In making a zero bath of the type described by Jones and Jacobson,[15] it was found necessary to reduce the ice to a fine state of division with an ice shaver, before a temperature of 0° could be obtained.

13 Carnegie Inst. Wash., Pub. No. 170, page 6, (1912).
14 Carnegie Inst. Wash. Pub. No. 198, (1914).
15 Amer. Chem. Journ., 40, 361, (1908).

Containing Vessels.—All bottles and measuring flasks were of Jena glass. After recalibrating the flasks by the weight method, the flasks and the bottles were allowed to stand partly filled with a solution of chromic acid for several weeks. During this time they were frequently shaken to insure thorough cleaning.

Solutions.

Water.—The water used in the preparation of the solutions was purified by the method of Jones and Mackey[16] as modified by Schmidt.[17] In no case was the specific conductivity greater than 1.7×10^{-6}.

Salts.—In all cases, Kahlbaum's or Merck's best products were selected. These were recrystallized from conductivity water before they were used.

Standardization.—On account of the nature of the substances studied, it was necessary to standardize most of the solutions by analytical methods. These methods will be taken up briefly in connection with the discussion of the individual salts. Standardization by analytical means is open to the objection that solutions must stand for some time before the conductivity measurements are made. This vitiates results in the case of salts which are hydrolyzed or undergo slight decomposition in solution. In the first instance alkali resulting from hydrolysis will attack the glass container, as was shown by the etching of a Jena glass bottle in which a N/8 solution of trisodiumphosphate had been standing for several weeks. By standardizing as rapidly as is consistent with accuracy, and by keeping the solutions in a cool dark locker, these deleterious effects are minimized. From the solution which had been analyzed, the others were made by diluting with conductivity water. Care was taken that no volume less than 35 c.c. should be involved in these measurements.

Cell Constants.

The cell constants were frequently determined throughout this work, in the usual way, by means of a solution of pure potassium chloride. For the cells with electrodes some distance apart, a N/50 solution was used. The value found by Kohlrausch, 129.7 (Siemans units), at 25°, was taken for the molecular conductivity of this solution. For the cells having their electrodes closer together, a N/500 solution was employed. The molecular conductivity of this had been determined in a cell, the constant of which had been found by the use of the N/50 solution.

16 Amer. Chem. Journ., 19, 90, (1897).
17 Ibid, 17, 83, (1895).

Precautions.

Before proceeding to the experimental data and methods of calculating them, it may be well to call attention to a few precautions which, if taken, may be of some assistance to those engaged in work requiring apparatus and methods somewhat similar to those used in this investigation.

(a) Jacobson[18] has called attention to a method for the prevention of the collection of air bubbles on the electrodes at 25° and above. He recommends heating the cell and contents a few degrees higher than the temperature at which the conductivity is to be measured, and then cooling them down to the desired temperature. In the light of Shaeffer's[19] work, it is seen that in the case of certain salts—notably chromium compounds—such treatment brings about a change in conductivity which persists for months. Shaeffer's observation was verified in the course of the present investigation. It was noticed that the conductivity of a solution of ammonium chromate was somewhat different at 25° after standing in the 25° bath, from the conductivity of the same solution when brought to a temperature of 25° from 0° to 15°. It was found best to remove the bubbles by tilting the cells slightly and partly removing the electrodes. If this is done once or twice while the solutions are coming to temperature, no further collection of bubbles will be noticed.

(b) The first few cubic centimeters of conductivity water should be discarded from the siphon used in drawing the water from its container. The water remaining below the stopcock, is, to some extent, exposed to laboratory atmosphere, and if some time has elapsed since the removal of the last portion, considerable difference in conductivity will be noticed if the above precaution is neglected.

(c) All connections in the wiring system used with the conductivity apparatus, should be soldered where this will not injure the apparatus. When not in use, the ends of the wires for connecting the cells with the bridge should be protected by small glass tubes.

(d) The noise of the motor used for stirring the baths was found to interfere with the reading of the bridge. This trouble was, in a great measure, overcome by mounting the motor on heavy rubber sheeting and providing washers of the same material for all bolts used in holding this machine in place.

Results.

In the following tables, all conductivities are expressed in Siemen's units, and are molecular conductivities—gram—molecular

18 Amer. Chem. Journ., 40, 366, (1908).
19 Ibid, 49, 240, (1913).

weights having been used in preparing the solutions. The molecular conductivities (μ_v) were calculated from the equation $\mu_v = K \frac{Va}{Rb}$; where K is the cell constant, V the volume concentration, R the resistance indicated on the rheostat, (a) and (b) the two arms of the bridge. The percentage dissociation (α) was calculated from the equation $\alpha = \frac{100\ \mu_v}{\mu_\infty}$ where $\mu\infty$ is the highest value of μ_v obtained. The temperature coefficients in conductivity units were calculated from the formula—

$$\frac{(\mu_v)\ t_2 - (\mu_v)\ t_1}{t_2 - t_1} = \text{coefficient}$$

in which $(\mu_v)\ t_2$ represents μ_v at the higher temperature t_2 and $(\mu_v)\ t_1$ at the lower temperature (t_1). The coefficients expressed as percentages were calculated from this formula—

$$\frac{(\mu_v)\ t_2 - (\mu_v)\ t_1}{t_2 - t_1} \times \frac{100}{(\mu_v)\ t_1}$$

For every measurement in these tables, three bridge readings involving different values for R were made, and the mean of these readings was taken as the basis of calculation.

Sodium Bromate.

This salt was twice recrystallized and then was dried at 100° for several hours. After cooling over phosphorus pentoxide the required amount was weighed and put into solution.

MEASUREMENTS

TABLE I.

Molecular Conductnvity.

V	0°	15°	25°
8	42.77	63.62	78.84
16	44.94	67.03	83.38
32	47.49	70.72	87.95
128	49.64	74.39	92.67
512	52.69	78.76	96.53
1024	53.10	79.59	99.26
2048	58.27	85.45	105.1
4096	61.10	83.34	105.3

TABLE II.

Percentage Dissociation.

V	0°	15°	25°
8	69.9	74.4	74.8
16	73.5	78.4	79.1
32	77.7	82.7	83.5
128	81.2	87.0	88.0
512	86.2	92.1	91.6
1024	86.9	93.1	94.2
2048	95.3	100.	99.5
4096	100.		100.

TABLE III.

Temperature Coefficients.

	0 to 15°		15° to 25°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.
8	1.38	3,22	1.52	2.39
16	1.47	3.27	1.63	2.43
32	1.54	3.24	1.72	2.43
128	1.64	3.30	1.82	2.45
512	1.73	3.28	1.77	2.25
1024	1.76	3.31	1.96	2.47
2048	1.81	3.10	1.97	2.30
4096	1.48	2.42	2.19	2.63

SODIUM SULPHOCYANATE.

The original solution of this salt was standarized by treating a measured volume with a slight excess of an acidified solution, silver nitrate. The precipitate of silver sulphocyanate was filtered into a Gooch crucible, washed and weighed. Duplicate determinations were made as in the case of all solutions standardized by analysis.

TABLE IV.

Molecular Conductivity.

V	0°	15°	25°	35°
4	46.79	69.00	84.36	102.5
8	49.68	72.57	96.36	107.8
16	50.96	75.86	94.90	114.2
32	52.90	79.14	98.81	118.6
128	55.47	83.19	102.8	124.3
512	57.77	85.81	106.7	129.7
1024	57.67	86.50	107.8	130.9
2048	58.10	86.22	107.8	130.6

TABLE V.

Percentage Dissociation.

V	0°	15°	25°	35°
4	80.5	79.8	78.2	78.4
8	85.5	83.9	89.4	82.5
16	87.7	87.7	88.0	87.4
32	91.0	91.4	91.6	90.8
128	95.4	96.1	95.3	95.1
512	99.4	99.2	99.0	99.3
1024	99.4	100.	100.	100.
2048	100.0			

TABLE VI.

Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.	Cond. Units	Per cent.
4	1.48	3.16	1.53	2.22	1.82	2.15
8	1.52	3.05	2.38	3.27	1.15	1.19
16	1.65	3.23	1.91	2.51	1.93	2.03
32	1.74	3.28	1.97	2.48	1.98	2.00
128	1.84	3.31	1.96	2.35	2.15	2.09
512	1.86	3.21	2.09	2.44	2.29	2.14
1024	1.92	3.32	2.13	2.46	2.31	2.14
2048	1.87	3.21	2.16	2.50	2.28	2.11

SODIUM THIOSULPHATE.

Iodine which had been resublimed in the presence of potassium iodide was weighed into small flasks with tightly fitting glass stoppers. About 20 gm. of potassium iodide and 0.5 c.c. of water had been previously weighed into these flasks. After the weight of the added iodine was determined, the flasks were opened in Erlenmeyer flasks containing 200 c.c of water and potassium iodide. This solution was titrated with the thiosulphate. Starch solution was used as an indicator.

TABLE VII.

Molecular Conductivity.

V	0°	15°	25°	35°
4	77.90	115.3	143.3	172.6
8	82.52	129.8	160.8	196.0
16	94.10	143.4	178.4	214.8
32	103.0	153.2	193.0	235.0
128	113.1	172.4	214.9	259.9
512	126.0	189.0	234.0	283.8
1024	124.8	191.9	239.1	284.1
2045	128.1	194.1	241.1	284.3
4096	131.4	195.0	244.0	290.5

TABLE VIII.

Percentage Dissociation.

V	0°	15°	25°	35°
4	59.2	59.1	58.7	59.4
8	62.8	66.5	65.9	67.4
16	71.6	73.5	73.1	73.9
32	78.4	78.5	79.1	80.8
128	86.0	88.4	88.0	89.4
512	95.8	96.9	95.9	97.6
1024	94.9	98.4	97.9	97.7
2048	97.5	99.5	98.8	97.8
4096	100.	100.	100.	100.

TABLE IX.

Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.	Cond. Units	Per cent.
4	2.49	3.07	2.80	2.43	2.93	2.04
8	3.15	3.81	3.10	2.38	3.52	2.18
16	3.28	3.48	3.50	2.44	3.64	2.04
32	3.34	3.24	3.98	2.60	4.19	2.17
128	3.95	3.49	4.24	2.46	4.50	2.09
512	4.19	3.32	4.50	2.38	4.98	2.12
1024	4.47	3.58	4.70	2.45	4.50	1.88
2048	4.40	3.43	4.69	2.41	4.32	1.79
4096	4.23	3.22	4.90	2.50	4.65	1.90

SODIUM DITHIONATE.

After recrystallizing from conductivity water, 10 c.c. of the sodium dithionate solution were evaporated to dryness in a weighed platinum dish. After heating to a dull red for some time, the dish and contents were cooled over calcium chloride and weighed. From the weight of the sodium sulphate the strength of the original solution of sodium dithionate was calculated.

TABLE X.

V	0°	15°	25°	35°
8	91.28	135.9	167.8	202.6
16	99.71	147.6	183.9	220.3
32	107.8	161.7	200.5	241.6
128	121.4	180.9	225.0	272.5
512	130.6	195.6	242.8	293.9
1024	137.1	203.6	255.0	308.6
2048	139.1	208.4	259.4	314.3
4096	139.1	207.3	258.2	312.7

TABLE XI.

Percentage of Dissociation.

V	0°	15°	25°	35°
8	65.6	65.2	64.6	64.4
16	71.6	70.8	70.8	70.1
32	77.5	77.6	77.3	76.8
128	87.2	86.8	86.7	86.7
512	93.8	93.9	93.6	93.5
1024	98.6	97.7	98.3	98.1
2048	100.	100.	100.	100.

TABLE XII.

Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.	Cond. Units	Per cent.
8	2.97	3.00	3.18	2.34	3.49	2.08
16	3.19	3.19	3.63	2.45	3.64	1.97
32	3.59	3.33	3.88	2.40	4.11	2.04
128	3.96	3.26	4.49	2.40	4.75	2.11
512	4.33	3.31	4.72	2.41	5.11	2.10
1024	4.43	3.23	5.14	2.52	5.36	2.10
2048	4.61	3.31	5.10	2.44	5.49	2.11
4096	4.54	3.26	5.09	2.45	5.45	2.11

SODIUM PYROPHOSPHATE.

This salt was dehydrated and weighed after it had been recrystallized.

TABLE XIII.

Molecular Conductivity.

V	0°	15°	25°	35°
16	100.2	154.8	194.5	235.3
32	118.3	181.5	227.5	276.1
128	159.0	242.7	304.0	370.5
512	197.0	302.8	384.5	466.7
1024	211.0	327.0	410.9	508.9
2048	216.1	336.9	421.8	517.4
4096	219.7	344.5	428.5	523.4

TABLE XIV.

Percentage Dissociation.

V	0°	15°	25°	35°
16	45.6	44.9	45.3	44.9
32	53.8	52.6	53.0	52.7
128	72.3	70.4	70.9	70.8
512	89.6	87.9	89.7	89.1
1024	96.0	94.9	95.9	97.2
2048	98.3	97.7	98.4	98.8
4096	100.	100.	100.	100.

TABLE XV.

Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.	Cond. Units	Per cent.
16	3.63	3.62	3.97	2.56	4.08	1.73
32	4.20	3.55	4.60	2.53	4.86	1.76
128	5.57	3.49	6.13	2.52	6.64	2.18
512	7.51	3.81	8.17	2.69	8.22	2.13
1024	7.73	3.66	8.39	2.56	9.80	2.38
2048	8.05	3.72	8.49	2.52	9.56	2.26
4096	8.26	3.75	8.40	2.43	9.49	2.21

TRISODIUM PHOSPHATE.

All salts of orthophosphoric acid were treated in the same manner. After making a solution of approximately the required strength by weighing the salt, it was standardized by the method of Schmitz.[20] This differs from the usual method, in that the magnesium ammonium phosphate is precipitated in a hot solution, by the slow addition of ammonia to an acid solution of the phosphate, to which an excess of "magnesia mixture" had been previously added. A very pure, coarsely crystalline precipitate, which settles readily, is obtained by this method.

From the weight of magnesium pyrophosphate yielded by this precipitate on ignition, the strength of the solution of the sodium salt was calculated.

TABLE XVI.

Molecular Conductivity.

V	0°	15°	25°
32	120.5	195.3	254.2
128	163.7	261.7	338.1
512	185.2	292.8	361.5
1024	195.8	307.0	380.5

TABLE XVII.

Percentage Dissociation.

V	0°	15°	25°
32	61.5	63.6	66.8
128	83.6	85.2	88.8
512	94.6	95.3	95.0
1024	100.	100.	100.

TABLE XVIII.

Temperature Coefficients.

	0° to 15°		15° to 25°	
	Cond. Units	Per cent.	Cond. Units	Per cent.
32	4.98	4.13	5.89	3.01
128	6.53	3.98	7.64	2.91
512	7.17	3.87	6.86	2.34
1024	7.41	3.79	7.35	2.39

20 Zeit. anal. Chem. 45, 512, (1906).

SODIUM DIHYDROGEN PHOSPHATE.

The solution of this salt was standardized by the method discussed in connection with the trisodium phosphate.

TABLE XIX.

Molecular Conductivity.

V	0°	15°	25°	35°
8	31.02	47.47	59.79	72.40
16	33.75	51.62	64.45	79.55
32	36.16	55.24	69.25	84.25
128	40.13	60.98	75.39	93.67
512	43.00	65.52	81.59	99.90
1024	42.07	64.95	81.17	100.6

TABLE XX.

Percentage of Dissociation.

V	0°	15°	25°	35°
8	72.2	72.4	73.2	71.9
16	78.5	78.7	78.9	79.0
32	84.2	84.3	84.8	83.7
128	93.4	93.0	94.7	93.1
512	100.	100.	100.	99.3
1024				100.

TABLE XXI.

Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.	Cond. Units	Per cent.
8	1.09	3.52	1.23	2.59	1.26	2.10
16	1.19	3.52	1.28	2.48	1.51	2.34
32	1.27	3.51	1.40	2.53	1.50	2.16
128	1.38	3.43	1.44	2.36	1.80	2.42
512	1.50	3.46	1.60	2.45	1.83	2.24
1024	1.52	3.55	1.62	2.48	1.94	2.39

SODIUM TUNGSTATE.

The original solution of sodium tungstate was standardized by precipitating the tungstic acid as mercuros tungstate. On ignition, this yields the trioxide of tungsten which can be weighed.

TABLE XXII.

Molecular Conductivity.

V	0°	15°	25°	35°
4	59.56	100.2		
8	69.75	112.7	141.6	172.0
16	82.65	126.7	159.0	193.2
32	87.53	134.3	168.7	205.5
128	98.54	151.5	190.7	233.5
512	107.25	164.6	207.4	254.1
1024	108.67	167.3	211.4	255.2

TABLE XXIII.

Percentage Dissociation.

V	0°	15°	25°	35°
4	54.8	59.9		
8	64.2	67.3	66.9	67.3
16	76.1	75.7	75.2	75.7
32	80.6	80.3	79.8	80.5
128	90.7	90.5	90.2	91.4
512	98.7	98.3	98.1	99.5
1024	100.	100.	100.	100.

TABLE XXIV.

Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.	Cond. Units	Per cent.
4	2.71	4.55				
8	2.86	4.10	2.88	2.56	3.24	2.28
16	2.93	3.54	3.23	2.54	3.42	2.15
32	3.12	3.56	3.44	2.56	3.68	2.18
128	3.52	3.57	3.92	2.58	4.28	2.24
512	3.82	3.56	4.28	2.60	4.67	2.25
1024	3.90	3.56	4.41	2.63	4.38	2.07

SODIUM FORMATE.

In a cold acid solution, permanganate acts only slowly with formic acid, while in a hot solution the latter is lost by volatization. In spite of statements to the contrary, oxidation by means of permanganate in an alkaline solution is a most unsatisfactory process. This led to the use of an indirect method of standardization for the sodium formate solution. An excess of standard permanganate solution was measured from a burette into an alkaline solution of the formate. After standing for some time, a known weight of pure sodium oxalate was added. The solution was then acidfied and heated. A standard solution of permanganate was used to titrate this in the usual way. The total amount of permanganate less that which is equivalent to the sodium oxalate is the permangnate used for the oxidation of the solution formate.

TABLE XXV.

Molecular Conductivity.

V	0°	15°	25°	35°
4	56.09	84.34	105.0	126.4
8	62.13	91.91	113.6	140.1
16	64.75	97.82	121.4	147.4
32	67.72	99.10	130.2	157.1
128	72.48	109.8	137.7	166.3
512	74.63	109.6	139.1	166.7
1024	75.65	112.8	140.9	181.0
2048	78.68	114.8	147.9	184.7
4096	79.73	118.7	148.1	184.1

TABLE XXVI.

Percentage Dissociation.

V	0°	15°	25°	35°
4	70.3	71.0	70.9	68.6
8	77.9	77.4	76.7	76.0
16	81.2	82.4	81.9	80.0
32	84.9	83.5	87.9	85.3
128	90.9	92.5	92.9	90.3
512	93.6	92.4	93.9	90.5
1024	94.8	95.0	95.1	98.3
2048	98.7	96.7	99.8	100.
4096	100.	100.	100.	

TABLE XXVII.

Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.	Cond. Units	Per cent.
4	1.88	3.35	2.07	2.45	2.14	2.03
8	1.84	2.96	2.16	2.35	2.65	2.33
16	1.53	2.36	2.35	2.41	2.60	2.14
32	2.09	3.08	3.11	3.13	2.69	2.00
128	2.48	3.42	2.80	2.55	2.86	2.07
512	2.35	3.14	2.95	2.69	2.76	1.99
1024	2.47	3.26	2.81	2.49	4.01	2.84
2048	2.41	3.06	3.31	2.88	3.68	2.49
4096	2.59	3.24	2.94	2.49	3.60	2.43

SODIUM CHROMATE.

The original solution of this salt was standardized by precipitating the chromium as mercurous chromate, by means of a solution of mercurous nitrate. On ignition, the mercurous chromate leaves a residue of chromic oxide which can be weighed.

TABLE XXVIII.

Molecular Conductivity.

V	0°	15°	25°	35°
4	74.76	113.4		
8	83.56	125.3	156.5	187.9
16	90.74	137.8	171.3	207.6
32	98.16	148.6	185.1	224.3
128	110.40	168.4	206.7	252.2
512	118.32	176.2	219.5	270.1
1024	114.60	173.6	216.9	262.3

TABLE XXIX.

Percentage Dissociation.

V	0°	15°	25°	35°
4	63.2	64.3		
8	70.6	71.1	71.3	69.6
16	76.7	78.2	78.0	76.8
32	82.9	84.3	84.3	83.0
128	93.3	95.5	94.2	93.4
512	100.	100.	100.	100.
1024				

TABLE XXX.

Temperature Coefficients.

V	0° to 15° Cond. Units	0° to 15° Per cent.	15° to 25° Cond. Units	15° to 25° Per cent.	25° to 35° Cond. Units	25° to 35° Per cent.
4	2.57	3.43				
8	2.78	3.32	3.12	2.48	3.14	2.00
16	3.13	3.44	3.35	2.43	3.63	2.11
32	3.36	3.42	3.65	2.45	3.92	2.11
128	3.86	3.49	3.83	2.27	4.55	2.20
512	3.85	3.25	4.33	2.45	5.06	2.30
1024	3.92	3.42	4.33	2.49	4.54	2.09

SODIUM DICHROMATE.

The same method of standardization was used in the case of sodium dichromate as was employed with the chromate.

TABLE XXXI.

Molecular Conductivity.

V	0°	15°	25°	35°
8	92.18	136.5		
16	96.57	143.5	176.3	211.4
32	101.25	148.4	182.7	219.5
128	106.8	158.3	194.7	233.5
512	106.1	158.3	194.4	234.6

TABLE XXXII.

Percentage Dissociation.

V	0°	15°	25°	35°
8	87.2	86.22		
16	91.3	90.65	90.71	89.88
32	95.7	93.74	93.98	93.32
128	100.	100.	100.	100.
512				

TABLE XXXIII.

Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.	Cond. Units	Per cent.
8	2.95	3.20				
16	3.13	3.24	3.28	2.28	3.51	1.99
32	3.14	3.10	3.43	2.31	3.68	2.01
128	3.43	3.21	3.64	2.29	3.88	1.99
512	3.50	3.31	3.61	2.28	4.02	2.06

POTASSIUM FERRICYANIDE.

This salt was dried for more than a month over phosphorus pentoxide. The solution was prepared by weighing the required amount of the dry salt, and dissolving in the usual manner.

TABLE XXXIV.

Molecular Conductivity.

V	0°	15°	25°	35°
8	158.6	230.2	282.1	
16	168.8	247.3	303.3	360.1
32	181.4	266.4	326.4	389.3
128	207.4	308.2	380.1	451.7
512	229.2	331.8	410.1	494.5
1024	238.1	354.5	438.9	529.9
2048	244.4	363.0	449.5	543.3
4096	254.5	375.3	465.8	564.3

TABLE XXXV.

Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.	Cond. Units	Per cent.
8	4.77	3.00	5.19	2.25		
16	5.23	3.09	5.60	2.26	5.68	1.87
32	5.66	3.11	6.00	2.25	6.29	1.92
128	6.71	3.23	7.19	2.33	7.16	1.88
512	6.83	2.98	7.87	2.37	8.40	2.04
1024	7.75	3.25	8.44	2.37	9.10	2.07
2048	7.90	3.23	8.65	2.38	9.38	2.08
4096	8.05	3.16	9.04	2.40	9.86	2.11

AMMONIUM IODATE.

A very dilute solution of the iodate, while cold, was carefully treated with sulphurous acid. When an amount sufficient to discharge the brown color due to free iodine had been added, the solution was warmed until the odor of sulphur dioxide could not be detected. The iodine was then determined as silver iodide.

TABLE XXXVI.

Molecular Conductivity.

V	0°	15°	25°	35°
16	48.17	72.21	89.97	108.5
32	50.51	76.35	94.93	114.6
128	54.34	81.32	101.1	122.2
512	56.54	85.07	106.2	128.6
1024	56.60	84.93	105.9	128.0
2048	55.99	83.92	104.6	127.2

TABLE XXXVII.

Percentage Dissociation.

V	0°	15°	25°	35°
16	85.1	84.88	84.7	84.4
32	89.2	89.74	89.4	89.1
128	96.0	95.59	95.2	95.0
512	99.9	100.	100.	100.
1024	100.			

TABLE XXXVIII .

Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.	Cond. Units	Per cent.
16	1.60	3.32	1.77	2.45	1.85	2.05
32	1.72	3.40	1.85	2.43	1.97	2.07
128	1.79	3.29	1.97	2.43	2.11	2.08
512	1.90	3.35	2.12	2.49	2.24	2.10
1024	1.88	3.32	2.10	2.47	2.21	2.08
2048	1.86	3.32	2.07	2.46	2.26	2.16

AMMONIUM DIHYDROGEN PHOSPHATE.

This solution was standardized in the same way as described in connection with sodium phosphate.

TABLE XXXIX.

Molecular Conductivity.

V	0°	15°	25°	35°
4	37.56	56.27	69.66	83.53
8	41.18	61.73	76.50	92.71
16	44.45	66.55	82.57	99.90
32	46.72	70.65	87.73	106.48
128	50.74	76.21	94.89	114.75
512	53.39	81.01	99.73	121.2
1024	56.50	83.92	104.6	126.7

TABLE XL.

Percentage Dissociation.

V	0°	15°	25°	35°
4	66.4	67.0	66.5	65.9
8	72.8	73.5	73.1	73.1
16	78.6	79.3	78.9	78.8
32	82.6	84.1	83.8	84.0
128	89.8	90.8	90.7	90.5
512	94.5	96.5	95.3	95.6
1024	100.	100.	100.	100.

TABLE XLI.

Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.	Cond. Units	Per cent.
4	1.24	3.30	1.34	2.37	1.38	1.98
8	1.36	3.30	1.47	2.39	1.62	2.11
16	1.47	3.30	1.60	2.40	1.73	2.09
32	1.59	3.40	1.70	2.41	1.87	2.13
128	1.69	3.33	1.86	2.45	1.98	2.09
512	1.83	3.42	1.87	2.31	2.15	2.15
1024	1.83	3.23	2.07	2.46	2.21	2.11

AMMONIUM CHROMATE.

The method used for standardization was identical with that used for standardizing the chromate of sodium.

TABLE XLII.

Molecular Conductivity.

V	0°	15°	25°	35°
4	93.63	137.		
8	102.5	149.8	181.9	215.4
16	110.5	163.1	199.5	236.7
32	119.1	176.3	215.4	257.2
128	135.1	201.2	247.1	292.7
512	144.6	213.2	262.2	312.7
1024	143.0	212.6	261.7	312.3

TABLE XLIII.

Percentage Dissociation.

V	0°	15°	25°	35°
4	64.7	64.2		
8	70.8	70.3	69.3	68.8
16	76.4	76.5	76.0	75.7
32	82.3	82.7	82.1	82.2
128	93.4	94.3	94.2	93.6
512	100.	100.	100.	100.

TABLE XLIV.

Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.	Cond. Units	Per cent.
4	2.89	3.08				
8	3.15	3.07	3.21	2.14	3.35	1.88
15	3.50	3.16	3.64	2.23	3.72	1.89
32	3.81	3.19	3.91	2.21	4.18	1.94
128	4.40	3.25	4.59	2.28	4.56	1.84
512	4.57	3.16	4.90	2.29	4.95	1.88
1024	4.63	3.23	4.91	2.30	5.06	1.93

AMMONIUM SULPHOCYANATE.

The amount of sulphocyanate present in the original solution was found by weighing the silver sulphocyanate formed on treating a portion of the solution with silver nitrate.

TABLE XLV.

Molecular Conductivity.

V	0°	15°	25°	35°
4	60.46	86.53	106.0	125.7
8	61.47	89.84	110.3	131.7
16	63.58	93.60	114.4	137.5
32	66.30	97.48	119.5	143.4
128	68.58	101.2	124.2	148.9
512	71.74	105.2	129.0	154.5
1024	72.00	105.2	129.2	154.8

TABLE XLVI.

Percentage Dissociation.

V	0°	15°	25°	35°
4	83.9	82.2	82.0	81.2
8	85.3	85.3	85.3	85.0
16	88.3	88.9	88.5	88.8
32	92.0	92.6	92.5	92.6
128	95.2	96.2	96.1	96.2
512	99.6	100.	99.8	99.8
1024	100.		100.	100.

TABLE XLVII.

Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.	Cond. Units	Per cent.
4	1.73	2.86	2.05	2.37	1.97	1.89
8	1.89	3.07	2.04	2.27	2.14	1.94
16	2.00	3.14	2.08	2.22	2.31	2.01
32	2.07	3.12	2.20	2.26	2.39	2.00
128	2.17	3.16	2.29	2.26	2.47	1.99
512	2.23	3.10	2.48	2.35	2.55	1.97
1024	2.21	3.06	2.40	2.28	2.56	1.97

LITHIUM CHROMATE.

The chromate in this solution was determined as it was in the case of sodium chromate.

TABLE XLVIII.

Molecular Conductivity.

V	0°	15°	25°	35°
8	74.62	112.3	139.9	169.1
16	82.62	124.1	154.3	187.3
32	89.83	136.6	169.9	205.5
128	101.6	155.1	193.0	236.5
512	106.4	164.5	205.3	249.0
1024	108.1	166.0	206.2	250.3
2048	114.1	168.3	209.0	251.4

TABLE XLIX.

Percentage Dissociation.

V	0°	15°	25°	35°
8	65.4	67.3	66.9	67.2
16	72.4	74.3	73.8	74.5
32	78.7	81.8	81.3	81.7
128	89.0	92.9	92.3	94.0
512	93.2	98.5	98.2	99.0
1024	94.7	99.4	98.6	99.5
2048	100.	100.	100.	100.

TABL L.

Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.	Cond. Units	Per cent.
8	2.51	3.36	2.76	2.45	2.92	2.08
16	2.76	3.34	3.02	2.45	3.30	2.13
32	3.11	3.46	3.33	2.43	3.56	2.09
128	3.56	3.50	3.79	2.44	3.34	1.73
512	3.87	3.60	4.08	2.48	4.37	2.12
1024	3.85	3.59	4.02	2.42	4.41	2.13
2048	3.61	3.16	4.07	2.41	4.24	2.02

RUBIDIUM IODIDE.

The iodine was determined as silver iodide.

TABLE LI.

Molecular Conductivity.

V	0°	15°	25°	35°
4	68.40	97.08		
8	70.48	101.4	122.6	145.6
16	72.59	104.3	127.2	150.6
32	74.75	108.6	131.7	157.8
128	78.51	114.2	139.7	166.6
512	79.92	116.0	142.0	169.5
1024	80.08	117.1	143.1	170.8

TABLE LII.

Percentage Dissociation.

V	0°	15°	25°	35°
4	85.41	82.9		
8	88.0	86.6	85.6	85.2
16	90.6	89.0	88.8	88.1
32	93.3	92.7	92.0	92.3
128	98.0	97.5	97.6	97.5
512	99.8	99.0	99.2	99.2
1024	100.	100.	100.	100.

TABLE LIII.

Temperature Coefficients.

	0° to 15°		15° to 25°		25° to 35°	
V	Cond. Units	Per cent.	Cond. Units	Per cent.	Cond. Units	Per cent.
4	1.91	2.79				
8	2.06	2.92	2.01	1.98	2.30	1.87
16	2.11	2.90	2.29	2.19	2.34	1.83
32	2.25	3.01	2.31	2.12	2.61	1.98
128	2.38	3.03	3.57	3.12	2.69	1.92
512	2.40	3.00	3.60	3.11	2.75	1.93
1024	2.46	3.07	3.70	3.16	2.77	1.93

DISCUSSION OF RESULTS

Conductivities.

Electrical conductivity in solutions of electrolytes depends on the number of ions present and on the velocities of these ions. The velocities will depend upon the size and mass of the ion and upon the viscosity of the medium, other conditions being the same. This leads to the conclusion that a salt showing high conductivity must be dissociated into a great number of ions, or the ions in solutions must be of such size and mass that they have a great velocity.

It can be seen from the above tables that certain salts, notably trisodium phosphate, sodium pyrophosphate, ammonium chromate, and potassium ferricyanid, show very high conductivity. The first of these compounds is strongly hydrolyzed even at low temperatures. The breaking down of complexes by hydrolysis gives rise to a great number of ions also in the case of the pyrophosphate. It is interesting to compare the conductivity of the trisodium phosphate with that of the corresponding potassium compound. While both show very high conductivities at all temperatures, the conductivity of the potassium salt is greater than that of the sodium. We would expect this from the fact that the sodium salt crystallized with 12 molecules of water, indicating great hydration in solution; while the potassium salt has no water of crystallization, which indicates only slightly hydrated ions in solution. The ammonium chromate is somewhat similar to the unhydrated potassium salt mentioned above, in that it carries no water of crystallization, and would therefore be expected to show greater conductivity than the corresponding hydrated salts of sodium and lithium. The high values of μ for potassium ferricyanide is largely due to the geeat number of ions yielded by this compound .The work of Getman and Bassett[21] indicates the production of 6 ions in solutions of this salt. By comparing the conductivities of the chromates of ammonia and the alkan metals, it is found that they stand in the following order:

Potassium chromate, ammonium chromate, sodium chromate, lithium chromate.

Ammonium compounds, as a rule, show higher conductivity than the corresponding potassium salts. This does not seem to be true in the case of the chromates. The smaller conductivity of lithium compounds when compared with compounds of sodium,

21 Carnegie Inst. Wash., Pub. No. 60, page 46, (1907).

is usually attributed to the greater hydration of the lithium ion in solution, as indicated by the greater tendency of lithium salts to crystallize with water.[22] The chromate of lithium, however, crystallizes with 1 molecule of water, while the chromate of sodium contains 10 molecules. The work of Jones and Bassett[23] has shown that many substances have greater hydrating power than is indicated by the water of crystallization contained in them. Such may be the case with lithium chromate.

Rubidium iodide shows a higher conductivity than the iodides of the other alkali metals. Knowing that rubidium has a greater atomic volume than sodium or potassium, we might expect the conductivity to be lowered by a decrease in the velocity of the ion, due to their volume and mass. It should, however, be remembered, that the hydrating power of these compounds of the alkali metals, decreases with increasing atomic volume. Just as sodium salts are less hydrated than lithium, so rubidium compounds would be expected to hydrate less than potassium. Thus, an apparent exception is explained by the theory of hydration.

Dissociations.

As a means of determining the dissociation of salts in solution, the conductivity method is of great service, but it is far from perfect. Hydrolysis, hydration, and polymerization all militate against obtaining a true value for $\mu\infty$. Since most salts show one or more of the above-named phenomena, it is certain that dissociations calculated from conductivity data are in most cases simply close approximations.

As a rule, salts in aqueous solutions are more dissociated at low temperatures than at high. This is in accord with the Thompson-Nernst hypothesis to which reference has already been made. Some exceptions to this rule have been found by other investigators. Barium nitrate, cadmium iodide, lead nitrate, and uranyl acetate have been found to show an increase in dissociation at higher temperatures. Shaeffer[24] has called special attention to the anomalous behavior of tripotassium phosphate, and suggests, as a cause, abnormal exothermic heat of dissociation. A great number of the substances studied in the present investigation showed a slight decrease in dissociation with rise in temperature. Sodium bromate, sodium thiosulphate, trisodium phosphate, and lithium chromate showed a well-defined increase. Several compounds have almost identical dissociations at all temperatures used.

22 Carnegie Inst. Wash., Pub. No. 60, p. 46, (1907).
23 Amer. Chem. Journ., 33, 562, (1905).
24 Amer. Chem. Journ., 49, 249, (1913).

Temperature Coefficients.

It has been found that the increase in conductivity with rise in temperature is due primarily to the velocities with which the ions move. This velocity is governed by the viscosity of the medium and the volume and mass of the ion. It is well known that the general tendency of rise in temperature is to decrease viscosity, and also the volume and mass of the ion, if the ion is considered not as a charged atom or group of atoms, but as a charged nucleus plus molecules of water, which must be carried along in all migrations through the remainder of the solvent. Jones has given a number of proofs for the validity of this conception of ions. He has also shown that these complexes break down at higher temperatures. With these facts in mind, we would expect a greater increase in conductivity with rise in temperature in the case of strongly hydrated salts, than in the case of weakly hydrated substances. Taking the amount of water with which a substance crystallizes as indicative of the extent to which it is hydrated, it is found that all of the compounds referred to in the above tables are in accord with this conception, except potassium ferricyanide and ammonium chromate. Reference has been made to the work of Jones and Getman and Jones and Bassett, which throws some light on the dissociation of the complex ferricyanide and also shows that water of crystallization is not always indicative of the degree of hydration to which a compound is subject. While they proved that the ferricyanide is not hydrated, it is rather probable that the lithium chromate is, since lithium salts, as a class, have a much greater tendency to hydrate than the salts of sodium or potassium.

The temperature coefficients expressed in percentages decrease in every case with rise in temperature. They increase somewhat on dilution. This is especially noticeable with hydrated and hydrolyzed salts.

Jones[25] has pointed out the following general relations deduced from the study of a large number of data concerning temperature coefficients:

1. Those ions with the largest hydrating power have the largest temperature coefficients of conductivity.

2. Those substances having equal hydrating power have approximately the same temperature coefficients of conductivity.

3. At higher dilutions, the temperature coefficients of conductivity, for any given substance, are greater than at lower dilutions.

In the present investigation all of these relations have been found to hold, with the few apparent exceptions noted in the above discussion.

25 Amer. Chem. Journ., 34, 357, (1905).

SUMMARY

1. A brief sketch of the work done in this laboratory on the conductivity of aqueous solutions, together with a resume of the results obtained by Jones and his co-workers, has been given.

2. A few practical suggestions as to apparatus and methods of procedure are offered.

3. Eighteen more or less unusual salts were studied with reference to their conductivity, over a range of temperature from 0° to 35°. Their temperature coefficients of conductivity are expressed in two sets of units; and where it is possible their dissociation has been calculated.

4. The results of this investigation are, for the most part, in accord with the findings of other workers in this field. Three exceptions were found to the rule that dissociation decreases with rise in temperature. Two apparent exceptions to the rule that large temperature coefficients are indicative of great hydration are noted and possible explanations are offered.

BIOGRAPHY

Charles Watkins, the author of this dissertation, was born in Talbott, Jefferson County, Tennessee, November 11th, 1885. To his mother, he is indebted for his earlier training. In 1905 he completed the course offered by the high school of Morristown, Tennessee, and in September of the same year enterd Washington and Lee University. From this institution he received the degree of Bachelor of Arts in 1909.

After he had been awarded the degree, Master of Science, by Vanderbilt University of Nashville, Tennessee in 1911, he returned to Washington and Lee University where he was instructor in chemistry until the fall of 1914, when he entered Johns Hopkins University as a graduate student in chemistry. His subordinate subjects have been physical chemistry and mineralogy.